

# Advances in Tribological Properties of Lubricating Anti-wear Agents

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**Abstract:** This paper reviews the latest research progress of lubricating anti-wear agents, discusses the application background, advantages and disadvantages of anti-wear agents, and analyzes the tribological properties of new anti-wear agents in recent years. The development of environmentally friendly and high-efficiency lubricant anti-wear agents is particularly important in the context of the strategic promotion of the "dual-carbon" policy. This paper provides new ideas and directions for the sustainable development of lubricant anti-wear agents through in-depth analysis of the performance of traditional anti-wear agents and analysis of new anti-wear agents.

**Keywords:** Lubricating Anti-wear Agents; Nano-lubrication; Ionic Liquids; Tribological Properties.

## 1. Introduction

Lubricant additives are key functional materials that determine the final performance of the lubricant. The content of additives is very small, but they can play a key role in changing the existing performance of the lubricant so that it can satisfy the normal operation of machinery and equipment and give the lubricant new performance. The global lubricant additives market size reached 110.24 billion yuan in 2023, while the Chinese lubricant additives market size reached 52.033 billion yuan [1]. This indicates that China has a considerable share in the global lubricant additives market and there is a great demand for lubricant additives in China. Lubricant additives include anti-wear agents, viscosity index improvers, pour point depressants and antioxidants. Anti-wear agents play an important role in lubricants by providing protection to machinery and equipment under a variety of operating conditions. The key role of anti-wear agents is to promote the formation of surface deposition films under normal operating conditions, a process that is effective in mitigating moderate wear. However, despite their significant advantages, there are some drawbacks. First of all, most of the anti-wear agents used in China contain phosphorus (P), sulfur (S) and other elements, these components may react with other additives in the lubricant at high temperatures to generate sulfate and phosphate, which will corrode the mechanical equipment and cause environmental pollution; some anti-wear agents do not have satisfactory performance at high temperatures, for example, sulfur-containing anti-wear agents are easy to decompose at high temperatures, resulting in a decline in anti-wear performance; different additives may occur incompatibility phenomenon, affecting the overall performance of the lubricant [2]; Some high-performance anti-wear agents have high costs and are not practical; because some anti-wear agents contain toxicity and poor biodegradability, they pose a threat to human health and are not conducive to environmental protection; and some anti-wear agents are prone to decomposition or precipitation during storage, transport and use, which shortens the life cycle of the lubricant. Therefore, the research and development of environmentally friendly new, efficient and low-cost anti-wear agents is the current research hotspot, in

order to adapt to the increasingly stringent environmental requirements and market demand.

## 2. Conventional Lubricants and Anti-Wear Agents

### 2.1. Nitrogen-containing Heterocyclic Borate Lubrication

Nitrogen-containing hybrid compounds and boron-containing organic compounds are of interest because of their excellent anti-wear, friction-reducing, and corrosion-resistant properties, as well as their anti-rust and non-toxic properties. In recent years, nitrogen-containing heterocyclic borates, as a class of environmentally friendly additives, have become a hot research topic because of their excellent thermal stability, anti-wear and friction reduction properties, and corrosion resistance. However, the only shortcoming of such compounds is that they are susceptible to hydrolysis, which not only weakens their original wear-reducing properties, but also their decomposition products may cause corrosion to the friction surface [3]. It is particularly important to introduce a new type of green lubricant additive aimed at preventing the hydrolysis of borate esters and enhancing the overall performance of the additive. The synthesis of this additive not only prevents the hydrolysis of borate esters but also improves their performance. Given the abundance of boron resources in China and the low cost of raw materials for the synthesis of borate esters, its application in the field of lubricant additives is very promising.

### 2.2. Nano-lubrication

Nano-lubrication technology, as an emerging high technology in the 21st century, plays an increasingly important role in the field of tribology. The unique properties of nanomaterials, including interfacial and surface effects, quantum size effect, small size effect, and macroscopic quantum tunneling effect, endow them with properties beyond traditional materials in optics, thermology, magnetism, mechanics and chemistry [4]. These properties make the nano-lubrication materials show significant advantages in reducing the friction coefficient, enhancing the wear-resistant performance and realising the self-repairing function, which

provide the surface lubrication of mechanical parts with a broad application prospect of improving the friction and wear, prolonging the service life and enhancing the mobility performance. In the research field of nano-lubricating additives, including nano-metal powders, hybrid additives of nano-metal powders and inorganic compounds, inorganic-based additives, as well as carbon nanotubes and fullerenes, show great potential as lubricating additives. In particular, nano-metal powders, such as copper, zinc, and brass powders, which form a pressure-bearing skeleton in the lubricant, effectively improve lubrication performance and reduce the coefficient of friction. Mixed additives of nano-metal powders with inorganic compounds, such as nano-copper and rare earth compounds, have shown good tribological properties for friction of different materials in engines. Inorganic compounds additives, such as nano-fluorinated rare earths, diamond-graphite powders, and nano-sized boron oxides, have attracted attention for their excellent extreme pressure and tribological properties. Carbon nanotube and fullerene additives have reduced coefficient of friction and enhanced extreme pressure properties in lubricants due to their unique molecular structure and excellent pressure resistance [5]. Although nano-lubricant additives have shown significant friction reduction and tribological properties, their mechanism of action has not been fully elucidated. Current research is mainly based on the "ball-bearing" theory of action, the thin-film theory and the repair theory [6]. Under low load conditions, nanoparticles may act as micro-bearings, while under high load conditions, they may form an oil film to reduce wear or even fill micro-scratches on surfaces to reduce wear. However, nano-lubricant additives face the problem of insufficient dispersion stability of micro- and nanoparticles in practical applications, which needs to be solved by careful selection of surface modifiers and improvement of modification process methods [7]. In addition, the preparation process of nanoparticles is more complicated and unfavourable for industrial mass production, so there is an urgent need to develop new preparation techniques to reduce the cost.

### 2.3. Ionic Liquid Lubrication

Ionic liquids, as a class of molten salt systems that are liquid at or near room temperature, show great potential in the field of lubricants due to their unique low melting point, low vapour pressure, adjustable polarity and safe and stable physicochemical properties. The lubrication mechanism of ionic liquids involves physical adsorption, friction chemical reaction and adsorption by special bipolar structures. Ionic liquids generally have better solubility in polar oils, while in non-polar oils the structure of cations and anions significantly affects their solubility. Ionic fluids with excellent tribological properties tend to contain active elements in both polar and non-polar oils. In addition, the compounding of ionic liquids with other additives can have an impact on the performance of the lubricant [8]. Ionic liquids/functionalized graphene oxide can be stably dispersed in water and form chemisorbed films on metal surfaces, thus reducing corrosion and improving tribological properties [9]. However, safety issues of ionic liquids, including their biodegradability and toxicity, as well as their corrosive effect on lubricating interfaces and oxidative stability at high temperatures, have been the focus of research. Conventional halogen-containing ionic liquids such as BF<sub>4</sub><sup>-</sup> and PF<sub>6</sub><sup>-</sup> are prone to produce toxic by-products, which not only aggravate the wear of the equipment but also

accelerate the corrosion of the friction sub. As a result, researchers are gradually turning their attention to the development of halogen-free ionic liquids. The tribological properties of halogen-free ionic liquids improve with increasing alkyl chain length and exhibit better performance than conventional lubricants at high temperatures [10]. Meanwhile halogen-free ionic liquids are valued for their environmental friendliness and low toxicity, and related research is expected to continue to grow in the future. Future research will focus on optimising the chemical molecular design of ionic liquids, improving their corrosion and oxidation resistance, exploring synergies with other additives, developing suitable additives, and exploring green synthesis methods.

### 2.4. Liquid Crystal Lubrication

Liquid crystals, as an ordered fluid between solid and liquid, show their unique advantages in the field of lubrication. Not only do they offer high load carrying capacity and low shear resistance, but they can also be used to optimise frictional properties by controlling the molecular orientation through external conditions. Liquid crystal lubrication additives have been focussed on, including benzoic acid derivatives, azobenzenes and cholesteryl esters, and the lubricating efficacy of these additives has been demonstrated in base oils. The friction-reducing mechanism of liquid crystal additives involves strong interaction of liquid crystal molecules with solid surfaces, dynamic adsorption, the "bingo" effect, and longitudinal orientation along grooves on friction surfaces, which enhances the performance of the lubricant. In the past decade, the nematic liquid crystal 5CB (4-pentyl-4'-cyanobiphenyl) has attracted much attention due to its molecular ordering that can be achieved during friction either by an applied electric field or by a surface oriented layer. Recent studies have shown that the 1,3-diketone material EPND (1-(4-ethylphenyl)nonane-1,3-dione), as a new and efficient lubricant additive for 5CB, is particularly suitable for precision machinery with low loads and stringent requirements for low friction [11].

### 2.5. Gas Phase Lubrication

Gas lubricated bearings, as a kind of sliding bearing with gas as lubricant, have a wide range of application prospects in the field of ultra-precision machining and inspection. Gas lubrication technology has been widely used in machine tools, measuring instruments and other equipment due to its advantages of high precision, low power consumption and long working life. The advantages of gas-lubricated bearings are their low frictional wear, wide operating temperature range, high rotary accuracy, and adaptability in special environments. However, gas lubricated bearings have low load carrying capacity, low stiffness, and high requirements for machining accuracy, gas hammer instability and eddy instability, and these limitations need to be overcome through further research and technology development.

### 3. Research Progress of New Anti-wear agents

#### 3.1. Novel Silicone Anti-wear Additives for Lubricants based on Quaternary Ammonium Salts of Dialkyl Dithiocarbamates.

The Institute of Petrochemical Synthesis of the Russian Academy of Sciences, presents a method for the preparation of anti-wear additives based on quaternary ammonium salts of dialkyl dithiocarbamates by non-catalytic interactions of stoichiometric amounts of the corresponding diamines, carbon disulfide, and tetraalkylammonium chloride in the presence of sodium hydroxide. All the synthesised additives were highly soluble in polyorganosilicone oils and at concentrations of 0.5-1.0 wt% they exhibited significant anti-wear activity as evidenced by a significant reduction in the diameter of the abrasion marks at the time of testing [12]. It has been shown that an increase in alkyl length in the anionic portion of the additive leads to more effective tribological properties, and the same trend is exhibited with an increase in the number of alkyl carbon atoms in the ammonium salt. The effect of additive concentration on the tribological properties of lubricating compositions has been investigated and the proposed additive type is a promising friction modifier for silicone lubricants.

#### 3.2. Late-model N, B, and P-co-doped Carbon dots as Additives for Friction-reduction and Anti-wear

Carbon dots (CD) are emerging carbon-based nanomaterials that are widely used as efficient lubricant additives to promote the tribological performance of green PEG-based lubricants. The synthesis of N, B,P-CDs does not involve any pre-processing or post-processing techniques. The simple "one-step" synthesis of state-of-the-art N, B,P co-doped CDs (N,B,P-CDs) with an amorphous structure of about 3.8 nm in diameter shows good potential for large-scale preparation, and the addition of N,B,P-CDs with suitable concentrations of N,B,P-CDs provides the friction-reducing, anti-wear, and load-supporting functions of PEG200 base oils. can be increased by a maximum of 38.1%, 86.2%, and 66.7%, respectively [13]. In addition, the tribological behavior of N, B, P-CD was significantly better than that of N, B-CD and P-CD under the same test conditions, showing the effect of synergistic polyatomic lubrication and excellent tribological performance.

#### 3.3. Phosphorus-free Triazine Organomolybdenum Friction Modifiers

Phosphorus-free triazinyl organomolybdenum compounds (DCDMs) in PAO10 base oils showed significant friction reduction and anti-wear properties. The results of the study showed that due to the synergistic effect between molybdenum (Mo) and sulphur (S), the DCDMs exhibited excellent tribological properties, with a reduction in the coefficient of friction of about 35% and a reduction in the diameter of the wear scars of about 46%. Further surface analyses revealed the formation of  $\text{MoO}_3$ ,  $\text{Fe}_2(\text{SO}_4)_3$ , FeS and  $\text{MoS}_2$  in the friction film, with the presence of  $\text{MoS}_2$  contributing most significantly to the enhanced friction reduction and tribological properties of the triazine-based organomolybdenum compounds [14].

### 3.4. Future Research Directions for Lubricating Anti-wear Agents

Against the backdrop of a national strategy to combat global climate change and realize the "dual carbon" goal, market demand for high performance, new environmentally friendly and long-life lubrication products continue to grow. With the deep integration of 5G, AI and IoT in the industrial sector, the demand for intelligent monitoring and remote maintenance will drive the intelligent development of energy-saving lubricating anti-wear agents. In the next 10 years, the market will focus on the development of products with features such as adaptive adjustment of lubrication performance and real-time failure warning to meet the demand for efficient and accurate lubrication in smart manufacturing. Synthetic organic anti-wear agents, due to their good high temperature resistance, corrosion resistance and good dispersibility, are used as cutting fluid additives in the petrol and diesel fields and in metal processing to reduce tool wear and improve machining efficiency. Future research will focus on the development of more efficient and environmentally friendly anti-wear products, such as nanomaterials, bio-based anti-wear agents, etc. These new anti-wear agents have advanced performance and more environmentally friendly production processes, which will help to reduce environmental pollution and meet the requirements of the national "dual-carbon" target, as well as the use of intelligent technology to improve the monitoring and maintenance of lubrication products. The use of intelligent technology to improve the monitoring and maintenance of lubrication products to adapt to the trend of intelligent manufacturing and sustainable development.

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